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Synthesis and investigation of catalytic activity of phenylene – And biphenylene bridged bimetallic Palladium-PEPPSI complexes

Fatma İmik, Sedat Yaşar*, İsmail Özdemir

Inönü University, Faculty of Science and Letter, Department of Chemistry, 44280, Malatya, Turkey

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ABSTRACT

A series of phenylene and biphenylene-bridged N-heterocyclic carbene (NHC) and their bimetallic NHC–Pd-PEPPSI complexes were reported and fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS, FTIR, and elemental analysis. The N tags with different electronic and steric properties were used on the synthesis of bridged bimetallic NHC–Pd-PEPPSI (PEPPSI: Pyridine Enhanced Precatalyst Preparation Stabilization Initiation) complexes. The catalytic properties of the bridged bimetallic NHC–Pd-PEPPSI complexes were investigated in the different C–C coupling reaction such as Suzuki-Miyaura reactions of aryl bromides with arylboronic acid, the Heck coupling reactions of aryl bromide with styrene and in the Sonogashira reactions of aryl bromides with phenylacetylene. Generally, all bridged bimetallic NHC–Pd-PEPPSI complexes showed good catalytic activity in the C–C coupling reactions.

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1. Introduction

After the first isolation of stable free *N*-heterocyclic carbene (NHC) by Arduengo, NHC have been an important ligand class in the design of homogeneous and heterogeneous catalysts due to their strong σ-donor bond character. The use of different electronically and sterically NHC lead to stronger and stable bonds with a metal center, which facilitates the catalytic performances [1], compared to classical ligands [2]. Recently, benzimidazolium ligands were used to the synthesis of many different metal–NHC–complex instead of imidazolium-based ligands because of the donation of extra stability to the metal NHC bond by benzimidazole ring [3]. The NHC complexes are preferred complexes in the many organic transformations reaction as a catalyst due to their unique catalytic features [4]. Pd–NHC complexes have a privileged place within NHC complexes. Pd–NHC complexes have gained enormous relevance in various C–C cross-coupling reactions such as Heck, Stille, Suzuki, Sonogashira, and Buchwald–Hartwig reactions for the synthesis of the different arylated product [5]. Many fine chemicals could be synthesized much more efficiently than before by this methodology. Arylated products are important for the synthesis of fine chemicals in the field of biologically active compounds, natural products etc [6]. There are many reports in the field of homogeneous catalysts for C–C cross-coupling reactions which are palladium catalyzed [7]. When these studies are examined, it is seen that monometallic Pd–NHC complexes are very common. However, bi- or polymetallic Pd–NHC complexes have been reported in recent years. Among these reports, a large number of bidentate bis-NHC ligands such as flexible alkyl [8], ether [9], benzyl [10], methylpyridine [11], picolly [12] and rigid linkers [13] and their Pd-complexes have been examined.

To better understand the catalytic behavior of bimetallic palladium complexes, we reported the synthesis and characterisation of bridged bis-benzimidazole based NHC and their bimetallic Pd-PEPPSI complexes and we implemented its activities on Suzuki-Miyaura, Heck and Sonogashira C–C cross-coupling reactions.

2. Results and discussions

2.1. Synthesis and characterisation

The preparation of bridged bis-*N*-heterocyclic carbene precursors from different N tags was presented in Scheme 1. These bis-benzimidazole NHC precursors were fully characterized by ^{1}H, ^{13}C NMR and elemental analyses. The reaction of N-substituted benzimidazole with *p*-xylyl dibromide or 2,2′-Bis(bromomethyl)-1,1′-

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* Corresponding author.
E-mail address: sedat.yasar@inonu.edu.tr (S. Yaşar).

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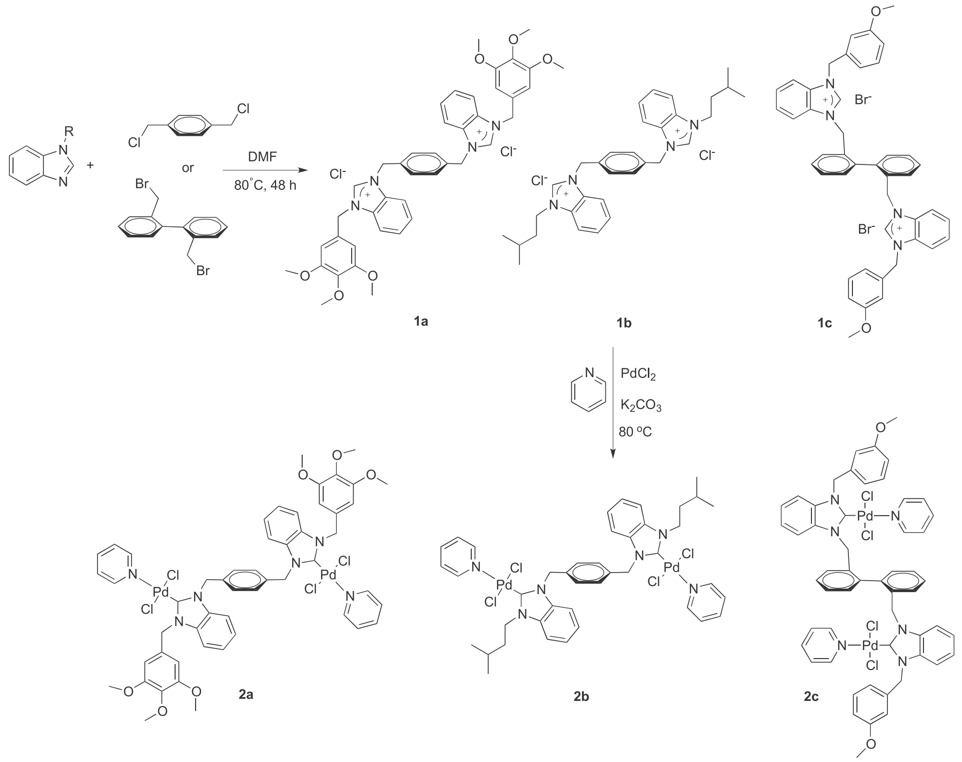


Scheme 1. Synthesis of bridged NHC salts (1a-c) and their bimetallic Pd-PEPPSI complexes (2a-c).

biphenyl in *N*,*N*-dimethylformamide (DMF) resulted in phenylene or biphennylene bridged bis-benzimidazolium salts (**1a**–**c**) (78–82%). The structure of bridged N-substituted benzimidazole salts **(1a-c)** was clearly confirmed by ^{1}H and ^{13}C spectra, where the NC***H***N hydrogens have low field shifts at 10.47, 11.61, 10.96 ppm, respectively in the ^{1}H NMR spectra and the N***C***HN carbons have also low field at 153.6, 143.2, 160.2 ppm, respectively in the ^{13}C NMR spectra. Results are similar to those previously reported [14]. In addition, in the FTIR, the $\nu_{(CN)}$ stretching frequency peaks of the bridged bis-*N*-heterocyclic carbene precursors were observed at 1560, 1556 and 1549 cm^{-1}, respectively for **1a-c**.

The preparation of bimetallic NHC–Pd-PEPPSI complexes was straightforward, starting from bis-NHC precursors **1a-c**. In a pressure tube, the reaction of **1a-c** with PdCl$_2$ and excess of K$_2$CO$_3$ in the presence of pyridine allowed the bimetallic PEPPSI-Pd-NHC complexes (**2a**–**c**), which can be purified by filtration on a short silica pad to afford an air- and moisture-stable light-yellow solid in 60–79% yield, respectively (Scheme 1). The structure of **2a**–**c** was confirmed by NMR, HRMS, IR spectroscopy and elemental analyses techniques. The ***C*₂** carbene carbon atoms of **2a-c** come to resonance in ^{13}C NMR spectra at $\delta = 164.7$, 163.7 and 164.7 ppm, respectively. The $\nu_{(CN)}$ stretching frequency peaks of the NHC–Pd-PEPPSI complexes was observed at 1407, 1413 and 1412 cm^{-1} in the FTIR, respectively for **2a-c**. The shifts in the stretching frequency of $\nu_{(CN)}$ are expected because of the electron flow from NHC to palladium metal. Unfortunately, we were not able to get a single crystal to perform X-ray diffraction of **2a-c** complexes.

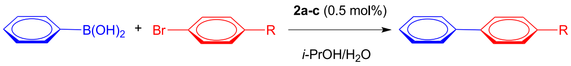
2.2. Catalysis

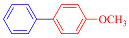
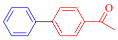
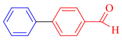
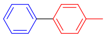
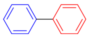
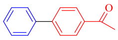
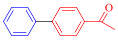
In order to demonstrate the catalytic activity of the bimetallic PEPPSI-Pd-NHC complexes, we decided to try three different model reactions to demonstrate the usability of complexes in different types of C–C cross-coupling reactions: the Suzuki-Miyaura of aryl bromides with phenylboronic acid, the Heck reaction of aryl bromides with styrene and the Sonogashira reaction of aryl bromides with phenylacetylene.

The Suzuki-Miyaura reaction is one of the most efficient and awarded methods for synthesis of arylated products which are highly valuable chemicals in many areas, under mild reaction condition from non-toxic comprehensive starting materials. The Suzuki-Miyaura reactions of aryl halides with boronic acid catalyzed by Pd-PEPPSI complexes was first reported by Organ and coworkers [15]. After that, the different type of Pd-PEPPSI complexes were tested on Suzuki-Miyaura reactions [16].

We tested the catalytic activity of **2a-c** in Suzuki-Miyaura reactions when performed at room temperature in 2-propanol/water (1:1 v/v) in the presence of K$_2$CO$_3$ by using an equimolecular amount of aryl halides (1 mmol) and boronic acid (1.1 mmol). The addition of water to C–C cross-coupling reactions as co-solvent may have significant profits. According to the literature [17], high polarity of water can have an accelerating effect on the oxidative addition of aryl halides as well as increase solubility of the base. In addition, the addition of water may be causing the displace of labile ligands such as especially iodide and bromide from the metal center. The C–C cross-coupling reaction in pure water is one of the major challenges. However, the low solubility of some substrates in water causing the use of aqueous solution as a solvent in reactions. Thus, several Suzuki-Miyaura reactions were performed in aqueous mixtures of DMF, *i*-PrOH, EtOH or CH$_3$CN. Herein, we choose the *i*-PrOH/water aqueous solutions due to our experience in this solvent mixture. In general, the complex **2a-c** showed good catalytic activity and afforded high yields with all aryl bromides but with 4-chloroacetophenone and 4-chloroanisol afforded very low yields (Table 1, entries 6,7). The higher yields were obtained with electron drawing group substituted aryl bromide such as 4-bromoacetophenone and 4-bromoaldehyde (Table 1, entries 1,2,3). From the results

Table 1
Suzuki-Miyaura cross-coupling reactions of phenylboronic acid catalyzed by **2a-c** complexes[a].2



Entry	Product	[catalyst]/yield (%)[b]		
		2a	2b	2c
1		80	86	83
2[c]		95	80	93
3		95	90	93
4		79	65	83
5		77	71	91
6[d]		25	10	18
7[d,e]		75	45	77

[a] Reaction condition: 0.5 mol% **2a-c**, 1 mmol p-R-C_6H_4Br, 1.1 mmol phenylboronic acid, 1.0 mmol K_2CO_3, rt, 1 h.
[b] Yields obtained by GC analysis using undecane as internal standard.
[c] Reaction carried out 30 min.
[d] Aryl chloride was used.
[e] Reaction carried out at 80 °C.

presented, it can be seen that our catalytic results in Suzuki-Miyaura reaction better than previously reported results although in those reported case the reactions proceeded in higher temperatures, catalyst loading and reaction times [18]. Among the complex **2a-c**, complex **2c** has a better catalytic activity in Suzuki-Miyaura reactions.

The Heck cross-coupling reaction was the first time announced by T. Mizoroki and R. F. Heck in 1971 and 1972 independently [19]. After that, synthesis of substituted olefins has emerged both academia and in industry. Despite the several Pd catalyzed Heck coupling reactions were reported [20], Pd–NHC complex catalyzed Heck coupling reaction in neat water or in aqueous mixtures or DMF are a few [21,22]. Thus, we want to show the utility of complex **2a-c** in Heck coupling reactions in aqueous reaction media. The Heck cross-coupling reaction between aryl bromides and vinylbenzene catalyzed by **2a-c** were summarized in Table 2. The reactions were carried out at 80 °C for 4 h in DMF/water (1:1 v/v) in the presence of K_2CO_3 and a catalyst loading of 0.3 mol%. In general, all complexes displayed good activity in the Heck coupling of aryl bromides with vinylbenzene but **2c** has better catalytic activity than rest. We think that these catalytic differences of **2a-c** may be due to inequality in the stability of the complexes. Ananikov et al. reported a useful mechanistic study for Pd–NHC catalyzed Heck reactions using many different types of NHC–Pd-PEPPSI complexes [23]. In this study, Pd-PEPPSI catalyzed Heck cross-coupling between aryl iodide or bromides and *n*-butylacrylate was investigated. Although styrene was used in our study, the high yields of the reactions with different aryl bromides indicate that our results can compete with Ananikov's results. At the same time, in many directions, our results are much better than the reported literature [24].

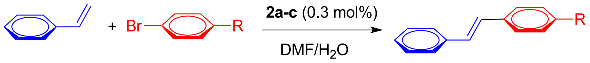
The reaction of aryl halides with alkynes to formed C(sp^2)-C(sp) called Sonogashira reactions. The reaction was first time reported by Sonogashira, Tohda, and Hagihara in 1975. This reaction is extremely powerful tools for synthesis nature product, biologically important chemicals, and fine chemicals which are called poly-functional alkynes and contain unsaturated C–C bonds [25]. After the discovery of Sonogashira reaction, many modifications have been made to on Sonogashira reaction to catch optimum yield by removing addition of Cu-salts [26], an addition of several additives [27], and using a different type of ligand [28]. Due to ligand plays a key role which generally stabilizes the active nano-palladium species, the most prominent of the modification is the use of different ligands in Sonogashira reaction. Another one is that perform the reaction absence of copper salts to prevent undesired Glaser type homocoupling product. Thus, the development of an efficient protocol under convenient ligand and copper and additive free condition for Sonogashira reaction is a remaining challenge.

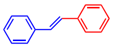
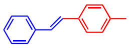
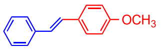
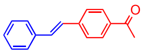
The Sonogashira cross-coupling reaction is one of the other C–C bond formation reaction catalyzed by **2a-c** we tried. The reactions were carried out at 120 °C for 1 h in DMF in the presence of *t*-BuOK and a catalyst loading of 0.3 mol%. The Sonogashira cross-coupling reaction between aryl bromides and phenylacetylene catalyzed by **2a-c** were summarized in Table 3. In general, all complexes displayed high catalytic activity with excellent yields in the Sonogashira coupling of aryl bromides with phenylacetylene. We attribute this high catalytic activity to the high stability of the complexes of **2a-c** in reaction media. However, if we compare the activity of bimetallic complexes with literature when reaction conditions in mind, the results indicate that our complexes performed better or moderate catalytic activity [29].

3. Conclusion

Herein, we reported and fully characterized three new phenylene or diphenylene linker bimetallic NHC–Pd-PEPPSI complexes. These bimetallic NHC–Pd-PEPPSI complexes were successfully tested as catalyst precursors in C–C cross-coupling reactions. When the catalytic activity of bimetallic NHC–Pd-PEPPSI complexes was compared with bimetallic counterparts,[14,24] these new bimetallic complexes performed a better catalytic activity in some C–C cross-coupling reactions. We attribute these catalytic differences to (i) the presence of extra metal in the catalyst precursor, give rise to some benefits into the catalytic reaction outcomes due to the higher local

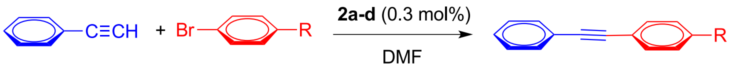
Table 2
Heck cross-coupling reactions of vinylbenzene catalyzed by **2a-c** complexes[a].10

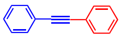
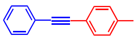
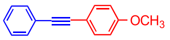
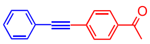


Entry	Product	[catalyst]/yield (%)[b]		
		2a	2b	2c
1		68	57	77
2		71	65	84
3		97	99	97
4		91	96	99

[a] Reaction condition: 0.3 mol⁄ **2a-c**, 1 mmol *p*-R-C_6H_4Br, 1.1 mmol phenylstyrene, 1.0 mmol K_2CO_3, 80 °C, 4 h.
[b] Yields obtained by GC analysis using undecane as internal standard.

Table 3
Sonogashira cross-coupling reactions of phenylacetylene catalyzed by **2a-c** complexes[a].5



Entry	Product	[catalyst]/yield (%)[b]		
		2a	2b	2c
1		>99	>99	98
2		94	90	88
3		90	87	83
4[c]		>99	>99	>99

[a] Reaction condition: 0.3 mol⁄ **2a-c**, 1 mmol aryl bromide, 1.1 mmol phenylacetylene, 1.0 mmol t-BuOK, 120 °C, 1 h.
[b] Yields obtained by GC analysis using undecane as internal standard.
[c] Reaction carried out 30 min.

concentration of the active metal in the bimetallic complex, (ii) high stability of the complexes during the catalytic reaction. The catalytic results showed that the complex **2a-c** has high activity in all C–C coupling reactions.

4. Experimental section

The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer with sample solutions prepared in $CDCl_3$ or DMSO-d_6. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. The HRMS (ESI) electrospray ionization mass spectra were recorded on a Shimadzu LCMS-IT-Toff spectrometer in $CH_3CN/CHCl_3$.The chemical shifts were reported in δ units downfield from the internal reference (Me_4Si). IR spectra were recorded with a PerkinElmer Spectrum 100 GladiATR FT/IR spectrometer. The catalytic products were characterized by a Shimadzu GC 2010-Plus contain HP-5 column (30 m, 0.32 mm, 0.25 mm). All products of the C–C coupling reactions are previously reported compounds.

4.1. Synthesis

4.1.1. p-xylyl-bis(N-(3,4,5-trimethoxybenzyl)benzimidazolium) dichloride, (1a)

A mixture of *N*-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazole (2 mmol) and 1,4-bis(chloromethyl)benzene (1.1 mmol) in dimethylformamide (DMF; 5 mL) was stirred and heated for 2 days at 80 °C. Diethyl ether (15 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethyl ether (3 × 10 mL) and dried under a vacuum to give the title

compound **1a** (630 mg, 82⁄) as white solid; m.p = 229.9 °C, $\nu_{C\text{-}N}$:1560.82 cm-1 [Found: C, 65.45; H, 5.84; N, 7.38. $C_{42}H_{44}N_4O_6Cl_2$ requires C, 65.37; H, 5.75; N, 7.26%]. ^1H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 2H, $NC\boldsymbol{H}N$), 8.15 and 7.98 (dd, 4H, J=8 Hz, $CH_2C_6\boldsymbol{H_4}CH_2$), 7.68–7.61 (m, 8H, $C_6\boldsymbol{H_4}$), 7.01 (s, 4H, $CH_2C_6\boldsymbol{H_2}(OCH_3)_3$-3,4,5), 5.82 (s, 4H, $C\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}$), 5.69 (s, 4H, $C\boldsymbol{H_2}C_6H_2(OCH_3)_3$-3,4,5), 3.77 (s, 12H, $CH_2C_6H_2(OC\boldsymbol{H_3})_3$-3,5), 3.65 (s, 6H, $CH_2C_6H_2(OC\boldsymbol{H_3})_3$-4). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.6 ($CH_2\boldsymbol{C_6}H_2(OCH_3)_3$-3,5), 143.2 ($N\boldsymbol{C_2}N$), 138.1, 135.1, 131.5, 131.3, 129.6, 129.4, 127.2, 114.6, 114.4, 106.9 (**C**, Aromatic carbons), 60.4 ($CH_2C_6H_2(O\boldsymbol{C}H_3)_3$-4), 56.6 ($CH_2C_6H_2(O\boldsymbol{C}H_3)_3$-3,5), 50.6 ($\boldsymbol{C}H_2C_6H_2\boldsymbol{C}H_2$), 49.9 ($\boldsymbol{C}H_2C_6H_2(OCH_3)_3$-3,4,5).

4.1.2. p-xylyl-bis(N-(iso-penthyl)benzimidazolium)dichloride, (1b)

The synthesis of **1b** was performed following the same procedure employed for the preparation of **1a**, starting from 2 mmol of *N*-(3,5-dimethylbenzyl)-5,6-dimethylbenzimidazole and 1.2 mmol of 1,4-bis(chloromethyl)benzene to give the title compound **1b** (441 mg, 80%) as white solide; m.p = 282.4 °C. $\nu_{(CN)} = 1556.18\ cm^{-1}$ [Found: C, 69.77; H, 7.44; N, 10.29. $C_{32}H_{40}N_4Cl_2$ requires C, 69.68; H, 7.31; N, 10.16%]. ^1H NMR (400 MHz, $CDCl_3$): δ 11.61 (s, 2H, $NC\boldsymbol{H}N$), 7.75–7.52 (m, 12H, $CH_2C_6\boldsymbol{H_4}CH_2$ and $C_6\boldsymbol{H_4}$), 5.87 (s, 4H, $C\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}$), 4.51 (m, 4H, $C\boldsymbol{H_2}CH_2\ CH(CH_3)_2$), 1.87 (m, 4H, $CH_2C\boldsymbol{H_2}CH(CH_3)_2$), 1.66 (m, 2H, $CH_2CH_2C\boldsymbol{H}(CH_3)_2$), 0.96 (d, 12H, $J = 4$ Hz, $CH_2CH_2CH(C\boldsymbol{H_3})_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2 ($N\boldsymbol{C_2}N$), 133.9, 131.3, 131.2, 129.6, 127.4, 127.2, 114.2, 112.8 (**C,** Aromatic carbons), 50.5 ($\boldsymbol{C}H_2C_6H_4\boldsymbol{C}H_2$), 46.3 ($\boldsymbol{C}H_2CH_2CH(CH_3)_2$), 38.0 ($CH_2\boldsymbol{C}H_2CH(CH_3)_2$), 26.0 ($CH_2CH_2\boldsymbol{C}H(CH_3)_2$), 22.3 ($CH_2CH_2\ CH(\boldsymbol{C}H_3)_2$).

4.1.3. 2,2′-Bis(N-(3-methoxybenzyl)methylbenzimidazolium)-1,1′-biphenyl diboromide, (1c)

The synthesis of **1c** was performed following the same procedure employed for the preparation of **1a**, starting from 1 mmol of *N*-(3-methoxybenzyl)benzimidazole and 1.2 mmol of 2,2′-Bis(bromomethyl)-1,1′-biphenyl to give the title compound **1c** (636 mg, 78%) as white solid; m.p = 223.8 °C, $\nu_{C\text{-}N}$: 1549.02 cm-1 [Found: C, 64.81; H, 5.07; N, 7.03. $C_{44}H_{40}N_4O_2Br_2$ requires C, 64.71; H, 4.94; N, 6.86%].

^1H NMR (400 MHz, $CDCl_3$): δ 10.96 (s, 2H, $NC\boldsymbol{H}N$), 7.67–6.86 (m, 24H, $C_6\boldsymbol{H_4}$, $CH_2C_6\boldsymbol{H_4}(OCH_3)$-3 and $C_{12}\boldsymbol{H_8}$), 6.10 and 5.70 (m, 8H, $C\boldsymbol{H_2}C_6H_4(OCH_3)$-3 and $C\boldsymbol{H_2}C_6H_4\ C_6H_4C\boldsymbol{H_2}$), 3.76 (s, 6H, $CH_2C_6H_2(OC\boldsymbol{H_3})$-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 ($CH_2\boldsymbol{C_6}H_4(OCH_3)$-3), (142.8 ($N\boldsymbol{C_2}N$), 138.5, 131.6, 131.0, 130.9, 130.2, 130.1, 129.6, 129.3, 129.1, 127.3, 127.2, 124.5, 114.7, 113.9 (**C,** Aromatic carbons), 55.3 ($CH_2C_6H_2(O\boldsymbol{C}H_3)$-3), 51.2 ($\boldsymbol{C}H_2C_6H_4C_6H_4\boldsymbol{C}H_2$), 49.9 ($\boldsymbol{C}H_2C_6H_2(OCH_3)_3$-3).

4.1.4. Tetrachloro[p-xylyl-bis(N-(3,4,5-trimethoxybenzyl) benzimidazol-2-ylidene]dipyridinedipalladium(II), (2a)

In the air, a pressure tube was charged with $PdCl_2$ (180 mg, 1 mmol), **1a** (1.1 mmol), K_2CO_3 (700 mg, 5 mmol) and 3 mL of pyridine. The reaction mixture was heated with vigorous stirring for 17 h at 80 °C then cooled to room temperature and diluted with dichloromethane (DCM). A short silica column was used for filtration. All volatiles were evaporated. Residue yellow solid was washed with hexane (2x10 mL) and diethyl ether (2x10 mL). Yellow solid was crystallized by DCM/Hexane (1:3) at room temperature to give the title compound **2a** (944 mg, 78%) as yellow solid; m.p = 255.8 °C. $\nu_{(CN)} = 1407.67$ cm-1 [Found: C, 51.67; H, 4.44; N, 7.04. $C_{52}H_{52}Cl_4N_6O_6Pd_2$ requires C, 51.55; H, 4.33; N, 6.94%]. ^1H NMR (400 MHz, DMSO): δ 8.91 (m, 4H, $C_5\boldsymbol{H_5}N$), 7.70 (m, 2H, $C_5\boldsymbol{H_5}N$), 7.56 (s, 4H, $CH_2C_6\boldsymbol{H_4}CH_2$), 7.30–7.01 (m, 12H, $C_5\boldsymbol{H_5}N$ and $C_6\boldsymbol{H_4}$), 6.83 (s, 4H, $CH_2C_6\boldsymbol{H_2}(OCH_3)_3$-3,4,5), 6.17 (s, 4H, $C\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}$), 6.09 (s, 4H, $C\boldsymbol{H_2}C_6H_2(OCH_3)_3$-3,4,5), 3.78 (s, 12H, $CH_2C_6H_2(OC\boldsymbol{H_3})_3$-3,5), 3.75 (s, 6H, $CH_2C_6H_2(OC\boldsymbol{H_3})_3$-4). ^{13}C NMR (100 MHz, DMSO): δ 164.7 ($N\boldsymbol{C_2}N$), 153.6, 153.3 and 151.2 ($CH_2\boldsymbol{C_6}H_2(OCH_3)_3$-3,4,5), 138.2, 137.7, 135.2, 134.5, 134.4, 130.7, 128.7, 125.0, 124.5, 123.5, 123.4, 111.6, 111.4, 105.1 (**C,** Aromatic carbons), 60.8 ($CH_2C_6H_2(O\boldsymbol{C}H_3)_3$-4), 56.6 ($CH_2C_6H_2(O\boldsymbol{C}H_3)_3$-3,5), 53.3 ($\boldsymbol{C}H_2C_6H_2\boldsymbol{C}H_2$), 52.9 ($\boldsymbol{C}H_2C_6H_2(OCH_3)_3$-3,4,5). HRMS (ESI+) for $C_{42}H_{42}N_4O_6Pd_2Cl_2$ (M − H): *m*/*z* calcd. 979.0567, found 979.0072.

4.1.5. Tetrachloro[p-xylyl-bis(N-(iso-penthyl)benzimidazol-2-ylidene]dipyridinedipalladium(II), (2b)

The synthesis of **2b** was performed following the same procedure employed for the preparation of **2a**, starting from **1b** to give the title compound **2b** % 70 (694 mg), as yellow solid; m.p = 278.8 °C. $\nu_{(CN)} = 1413.33$ cm-1 [Found: C, 50.97; H, 5.02; N, 8.64. $C_{42}H_{48}Cl_4N_6Pd_2$ requires C, 50.88; H, 4.88; N, 8.48%]. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.91$ (m, 4H, $C_5\boldsymbol{H_5}N$), 7.70 (m, 2H, $C_5\boldsymbol{H_5}N$), 7.52 (s, 4H, $CH_2C_6\boldsymbol{H_4}CH_2$), 7.34–7.01 (m, 12H, $C_5\boldsymbol{H_5}N$ and $C_6\boldsymbol{H_4}$), 6.09 (s, 4H, $C\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}$), 4.87 (m, 4H, $C\boldsymbol{H_2}CH_2\ CH(CH_3)_2$), 2.07 (m, 4H, $CH_2C\boldsymbol{H_2}\ CH(CH_3)_2$), 1.87 (h, 2H, $J = 6.6$ Hz, $CH_2CH_2\ C\boldsymbol{H}(CH_3)_2$), 1.08 (d, 12H, $J = 6.6$ Hz, $CH_2CH_2\ CH(C\boldsymbol{H_3})_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7 ($N\boldsymbol{C_2}N$), 151.2, 138.1, 135.2, 134.6, 134.2, 128.6, 124.5, 123.2, 123.1, 111.6, 110.3 (**C,** Aromatic carbons), 52.8 ($\boldsymbol{C}H_2C_6H_4\boldsymbol{C}H_2$), 47.0 ($\boldsymbol{C}H_2CH_2\ CH(CH_3)_2$), 38.2 ($CH_2\boldsymbol{C}H_2\ CH(CH_3)_2$), 26.2 ($CH_2CH_2\ \boldsymbol{C}H(CH_3)_2$), 22.6 ($CH_2CH_2CH(\boldsymbol{C}H_3)_2$). HRMS(ESI+) *m*/*z* for $C_{42}H_{48}N_6Pd_2Cl_4$ (M + Na+3H): calcd. 1018.0871, found 1018.2402. HRMS(ESI-) *m*/*z* for $C_{42}H_{48}N_6Pd_2Cl_2$ (M + Na−3H): calcd. 937.1066, found 937.1094.

4.1.6. Tetrachloro[2,2′-Bis(N-(3-methoxybenzyl)benzimidazol-2-ylidenemethyl)-1,1′-biphenyl]dipyridinedipalladium(II), (2c)

The synthesis of **2c** was performed following the same procedure employed for the preparation of **2a**, starting from **1c** to give the title compound **2**c (924 mg, 77%) as yellow crystal; m.p = 257.5 °C. $\nu_{(CN)} = 1411.99$ cm-1 [Found: C, 55.68; H, 4.19; N, 7.32. $C_{54}H_{48}Cl_4N_6O_2Pd_2$ requires C, 55.55; H, 4.14; N, 7.20%]. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.02$ (s, 4H, $C_5\boldsymbol{H_5}N$), 7.68–6.91 (m, 30H, $C_5\boldsymbol{H_5}N$, $C_6\boldsymbol{H_4}$, $CH_2C_6\boldsymbol{H_4}(OCH_3)$-3 and $C_{12}\boldsymbol{H_8}$), 6.50, 6.05 and 5.85 (m, 8H, $C\boldsymbol{H_2}C_6H_4(OCH_3)$-3 and $C\boldsymbol{H_2}C_6H_4\ C_6H_4C\boldsymbol{H_2}$), 3.81 (s, 6H, $CH_2C_6H_2(OC\boldsymbol{H_3})$-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.7 ($N\boldsymbol{C_2}N$), 159.5 ($CH_2\boldsymbol{C_6}H_4(OCH_3)$-3), 152.7, 152.1, 151.4, 139.9, 137.8, 134.8, 134.1, 133.2, 129.9, 129.5, 129.0, 128.2, 127.1, 124.4, 123.5, 122.9, 114.2, 111.3 (**C,** Aromatic carbons), 55.2 ($CH_2C_6H_2(O\boldsymbol{C}H_3)$-3), 53.5 ($\boldsymbol{C}H_2C_6H_4C_6H_4\boldsymbol{C}H_2$), 50.4 ($\boldsymbol{C}H_2C_6H_2(OCH_3)_3$-3). HRMS(ESI+) *m*/*z* for $C_{54}H_{48}Cl_2N_6O_2Pd_2Na_2$ (M+2Na−H): calcd. 1141.1007, found 1141.2774.

4.2. General procedure for the suzuki coupling reaction

Under the air, a 10 mL tube containing a stirring bar was charged with palladium catalyst (0.5 mol %, 0.005 mmol), potassium carbonate (138 mg, 1 mmol), aryl bromide (1 mmol), phenylboronic acid (135 mg, 1 mmol), isopropanol (2.0 mL), and water (2 mL). The mixture was stirred at room temperature for an appropriate time. The reaction was quenched with water, and the mixture was extracted with DCM. The organic phase was dried over $MgSO_4$, and filtered on short silica to remove palladium residue than filtrate analyzed by Gas Chromotography.

4.3. General procedure for the heck coupling reaction

Under the argon, a 10 mL Schlenk tube containing a stirring bar was charged with palladium catalyst (0.3 mol%, 0.003 mmol), potassium carbonate (138 mg, 1 mmol), aryl bromide (1 mmol), styrene (125 mg, 1.2 mmol), DMF (2.0 mL), and water (2 mL). The mixture was stirred at 80 °C for an appropriate time. The reaction was cooled to room temperature and quenched with water, and the mixture was extracted with DCM. Organic phase dried over $MgSO_4$ and filtered on short silica to remove palladium residue than filtrate analyzed by Gas Chromotography.

4.4. General procedure for the sonogashira coupling reaction

Under the argon, a 10 mL tube containing a stirring bar was charged with palladium catalyst (0.3 mol%, 0.003 mmol), *t*-BuOK (112 mg, 1 mmol), aryl bromide (1 mmol), phenylacetylene (115 mg, 1.1 mmol), DMF (2.0 mL). The mixture was stirred and heated at 120 °C for an appropriate time. The reaction was cooled to room temperature and quenched with water, and the mixture was extracted with DCM. Organic phase dried over $MgSO_4$ and filtered on short silica pad to remove palladium residue than filtrate analyzed by Gas Chromotography.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.019.

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